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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SONY CORP

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(72)Inventor : HORIE TAKESHI

**NODA KAZUHIRO**

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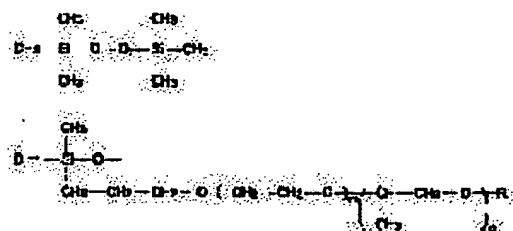
**(54) NONAQUEOUS ELECTROLYTE AND BATTERY USING THE SAME**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a nonaqueous electrolyte and a battery using it, having superior chemical stability and thermochemical stability.

**SOLUTION:** A negative electrode and a positive electrode are arranged facing each other via a separator, and a nonaqueous electrolyte intervenes between them.

The nonaqueous electrolyte includes a siloxane derivative represented by the general formula, and at least one kind of a light metal salt. The siloxane derivative is chemically stable and flame-retardant or low in vapor pressure, therefore it has superior thermochemical characteristic. In the formula, a represents an integer of 1 to 50, m represents an integer of 0 to 40, n represents an integer of 0 to 40, and R represents a hydrogen atom or an alkyl. Moreover, when same or different. Also, hydrogen atoms included in D and atoms.



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**Title:** JP2000058123A2: NONAQUEOUS ELECTROLYTE AND BATTERY USING THE SAME

**Country:** JP Japan

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**Inventor:** HORIE TAKESHI;  
NODA KAZUHIRO;  
YAMADA SHINICHIRO;

**Assignee:** SONY CORP  
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<p>(30) Priority:</p> <p>(43) Date of application publication: <b>25.02.00</b></p> <p>(84) Designated contracting states:</p>	<p>(71) Applicant: <b>SONY CORP</b></p> <p>(72) Inventor: <b>HORIE TAKESHI</b> <b>NODA KAZUHIRO</b> <b>YAMADA SHINICHIRO</b></p> <p>(74) Representative:</p>
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**(54) NONAQUEOUS  
ELECTROLYTE AND  
BATTERY USING THE  
SAME**

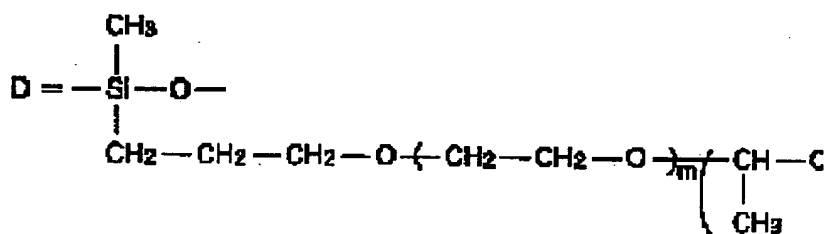
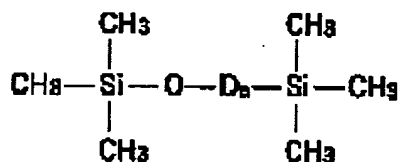
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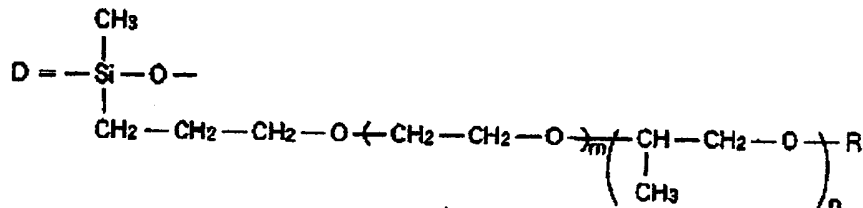
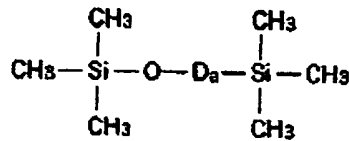
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【特許請求の範囲】

【請求項1】 下記の化1にて示されるシロキサン誘導体と、

\* 少なくとも1種の軽金属塩とを含むことを特徴とする非水電解液。

\* 【化1】



(式中、aは1から50の整数を表し、mは0から40の整数を表し、nは0から40の整数を表し、Rは水素原子またはアルキル基を表す。なお、a>1のときa個のDは同じでも異なってもよい。また、DおよびRに含まれる水素原子はハロゲン原子で置き換えられてもよい。)

【請求項2】 前記シロキサン誘導体は、温度25℃における動粘性率が5000cSt以下であることを特徴とする請求項1記載の非水電解液。

【請求項3】 前記シロキサン誘導体は、平均分子量が10000以下であることを特徴とする請求項1記載の非水電解液。

※

※【請求項4】 前記軽金属塩は、リチウム金属塩であることを特徴とする請求項1記載の非水電解液。

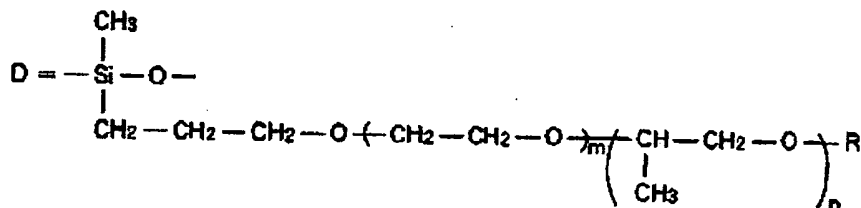
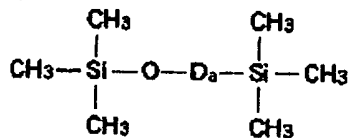
【請求項5】 温度25℃における導電率が0.1mS/cm以上であることを特徴とする請求項1記載の非水電解液。

【請求項6】 正極と、

負極と、

前記正極と前記負極との間に設けられたセパレータと、下記の化2にて示されるシロキサン誘導体および少なくとも1種の軽金属塩を含む非水電解液とを備えたことを特徴とする電池。

【化2】



(式中、aは1から50の整数を表し、mは0から40の整数を表し、nは0から40の整数を表し、Rは水素原子またはアルキル基を表す。なお、a>1のときa個のDは同じでも異なってもよい。また、DおよびRに含まれる水素原子はハロゲン原子で置き換えられてもよい。)

【請求項7】 前記非水電解液は、温度25℃における動粘性率が5000cSt以下のシロキサン誘導体を含むことを特徴とする請求項6記載の電池。

【請求項8】 前記非水電解液は、平均分子量が10000以下のシロキサン誘導体を含むことを特徴とする請求項6記載の電池。

【請求項9】 前記非水電解液は、温度25℃における導電率が0.1mS/cm以上であることを特徴とする請求項6記載の電池。

【請求項10】 前記正極は、リチウムイオンを吸蔵および脱離することができる酸化物もしくは硫化物を含むと共に、前記負極は、リチウム、リチウム合金あるいは

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リチウムイオンを吸蔵および脱離することができる炭素材料を含むことを特徴とする請求項6記載の電池。

【発明の詳細な説明】

【0001】

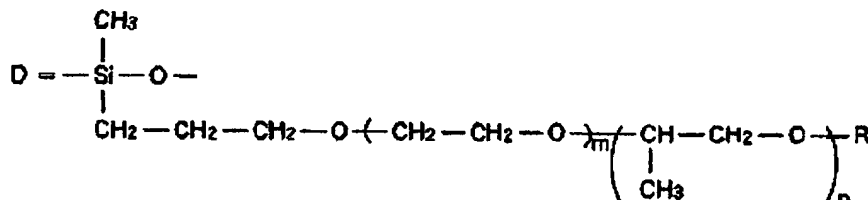
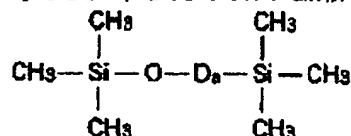
【発明の属する技術分野】本発明は、電解質である軽金属塩と溶媒とを含む非水電解液およびそれを用いた電池に関する。

【0002】

【従来の技術】近年になり、カメラ一体型ビデオテープレコーダ、携帯電話あるいはラップトップコンピュータなどの携帯用電気製品が急速に普及しつつある。また、環境問題の観点からNO<sub>x</sub>などの排気ガスを空气中に排出しない電気自動車の開発が社会的課題として取り上げられるようになってきた。このような状況の下、ポータブル電源およびクリーンなエネルギー源としての電池、特に、二次電池についての研究開発が活発に進められている。中でも、リチウム(Li)またはリチウムイオン(Li<sup>+</sup>)を用いた二次電池(リチウム二次電池)は、従来の水系電解液二次電池である鉛(Pb)二次電池またはニッケルカドミウム(Ni-Cd)二次電池と比較して高いエネルギー密度が得られるので、大きな期待を集めている。

【0003】このリチウム二次電池の電解液としては、低分子のエチレンカーボネートあるいはプロピレンカーボネートまたは炭酸ジエチルなどの炭酸エステルなどの非水溶媒に、電解質としてLiPF<sub>6</sub>などのリチウム系電解質塩を溶解させたものが、比較的導電率が高く、電位的にも安定であることから広く用いられている。

【0004】ところが、このような非水電解液を用いた\*



(式中、aは1から50の整数を表し、mは0から40の整数を表し、nは0から40の整数を表し、Rは水素原子またはアルキル基を表す。なお、a>1のときa個のDは同じでも異なってもよい。また、DおよびRに含まれる水素原子はハロゲン原子で置き換えられてもよい。)

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\*リチウム二次電池は高性能であるものの、可燃性の有機溶媒を電解液として用いているため、安全性において問題が起こる場合がある。例えば、電流の短絡時に急激に大電流が電池内に流れて発熱し、これにより有機溶媒を含む電解液が気化または分解を起こし、これによるガス発生のために、電池の破損、破裂あるいは発火が起こる可能性があった。そこで、従来は、これらを防止するために、電池内の圧力が上昇すると開裂する安全弁または電流遮断装置などを設けることにより安全対策を行っていた。

【0005】

【発明が解決しようとする課題】しかしながら、従来は、安全弁などの構造機構を改良することで安全性を確保していたので、構造が複雑となってしまおうと共に、それらの構造の分だけ電池の大きさが大きくなってしまおうという問題があった。そこで、電池材料を根本的に改善することが望まれている。

【0006】本発明はかかる問題点に鑑みてなされたもので、その第1の目的は、化学的安定性および熱化学的安定性に優れた非水電解液を提供することにある。

【0007】また、本発明の第2の目的は、電解液の気化または分解を抑制することにより、ガスの発生による電池の破損または発火を防止し、かつ電池性能に優れた電池を提供することにある。

【0008】

【課題を解決するための手段】本発明による非水電解液は、下記の化3にて示されるシロキサン誘導体と、少なくとも1種の軽金属塩とを含むものである。

【化3】

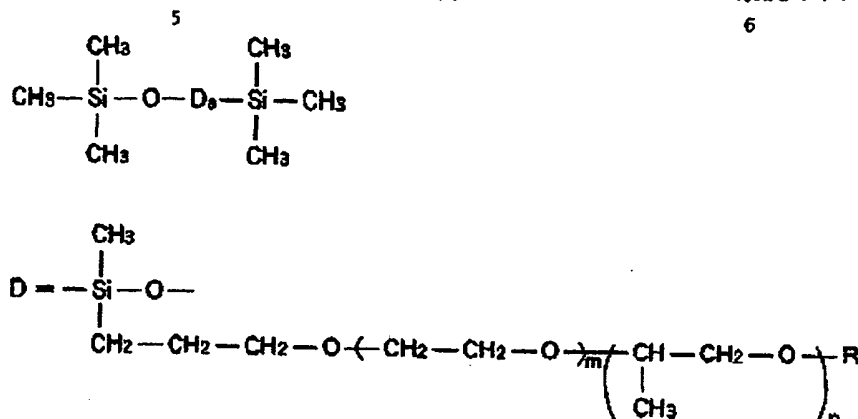
【0009】本発明による電池は、正極と、負極と、正極と負極との間に設けられたセパレータと、下記の化4にて示されるシロキサン誘導体および少なくとも1種の軽金属塩を含む非水電解液とを備えたものである。

【化4】

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(式中、aは1から50の整数を表し、mは0から40の整数を表し、nは0から40の整数を表し、Rは水素原子またはアルキル基を表す。なお、a>1のときa個のDは同じでも異なってもよい。また、DおよびRに含まれる水素原子はハロゲン原子で置き換えられてもよい。)

【0010】本発明による非水電解液では、化3に示したシロキサン誘導体を含んでいるので、化学的安定性が高く、難燃性または低蒸気圧であるために熱化学的にも優れるという特性を有している。よって、この非水電解液を用いて電池を構成すれば、電流の短絡時においても気化または分解が起こりにくく、電池の破損または発火が防止され、高電圧においても優れた電池性能が示される。

【0011】本発明による電池では、充電により非水電\*

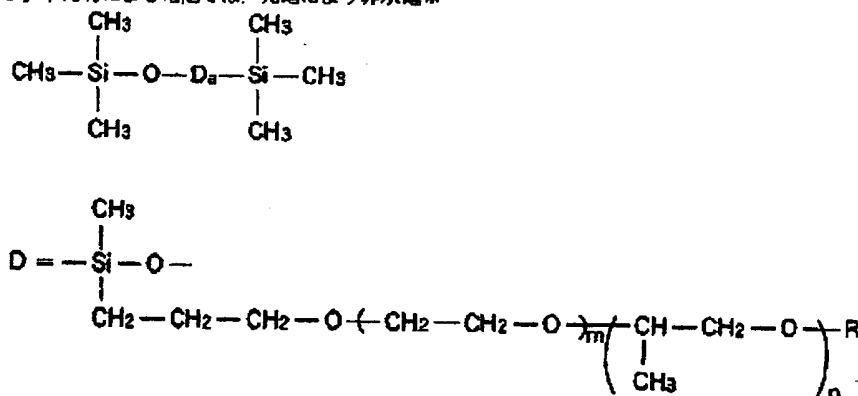
\* 解液中を軽金属イオンがセパレータを介して正極から負極へ移動し、放電により非水電解液中を軽金属イオンがセパレータを介して負極から正極へ移動する。ここでは、非水電解液が化4に示したシロキサン誘導体を含んでいるので、電流の短絡時においても気化または分解が起こりにくく、電池の破損または発火が防止され、高電圧においても優れた電池性能が示される。

【0012】

【発明の実施の形態】以下、本発明の実施の形態について図面を参照して詳細に説明する。

【0013】本発明の一実施の形態に係る非水電解液は、溶媒である化5に示したシロキサン誘導体と、電解質である少なくとも1種の軽金属塩とからなる。

【化5】



(式中、aは1から50の整数を表し、mは0から40の整数を表し、nは0から40の整数を表し、Rは水素原子またはアルキル基を表す。なお、a>1のときa個のDは同じでも異なってもよい。また、DおよびRに含まれる水素原子はハロゲン原子で置き換えられてもよい。)

【0014】このシロキサン誘導体は、珪素(Si)と酸素(O)との鎖状結合を基本骨格にもち、珪素に1価の有機基である側鎖が付加された鎖状型の無機高分子で

ある。このシロキサン誘導体は、化学的安定性が高く、難燃性または低蒸気圧であるために熱化学的安定性にも優れるという特性を有している。

【0015】なお、このシロキサン誘導体の温度25℃における動粘性率は5000cSt以下であり、平均分子量は10000以下であることが好ましい。電解液の溶媒として用いるには、粘度が比較的低く、かつ軽金属塩を溶解し得ることが必要だからである。これらは化5に示した化学式におけるDの側鎖基と化学式におけるa

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の数を適度に変換することにより調整される。その際、この化学式における $a$ は1から20の範囲内の整数であることが好ましい。

【0016】一方、軽金属塩にはリチウム塩あるいはナトリウム(Na)塩などのアルカリ金属塩またはアルミニウム(Al)塩などがあり、この非水電解液を使用する電池の種類に応じて便宜に選択される。例えば、リチウム電池を構成する場合には、 $\text{LiBF}_4$ 、 $\text{LiClO}_4$ 、 $\text{LiPF}_6$ 、 $\text{LiAsF}_6$ 、 $\text{CF}_3\text{SO}_2\text{Li}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 $\text{CF}_3\text{CO}_2\text{Li}$ 、 $(\text{CF}_3\text{CO}_2)_2\text{NLi}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 $(\text{C}_6\text{F}_5\text{SO}_2)_2\text{NLi}$ 、 $(\text{FSO}_2\text{C}_6\text{F}_5)(\text{CF}_3\text{SO}_2)\text{NLi}$ 、 $(\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{CLi}$ 、 $(\text{C}_6\text{F}_5)(\text{CF}_3)_2-3,5$ 、 $\text{BLi}$ あるいは $\text{LiCF}_3$ 、 $\text{LiAlCl}_4$ などのリチウム塩が使用される。

【0017】なお、この非水電解液の温度25℃における導電率は0.1mS/cm以上であることが好ましく、軽金属塩の種類あるいはその濃度により調整される。

【0018】また、この非水電解液は、シロキサン誘導体に加えて他の溶媒を含んでもよい。他の溶媒としては、例えば、プロピレンカーボネート、エチレンカーボネート、ジエチルカーボネート、メチルエチルカーボネート、1,2-ジメトキシエタン、1,2-ジエトキシエタン、γ-ブチロラクトン、テトラヒドロフラン、1,3-ジオキサラン、ジプロピルカーボネート、ジエチルエーテル、スルホラン、メチルスルホラン、アセトニトリル、プロピオニトリル、アニソール、酢酸エステルあるいはプロピオン酸エステルなどがあり、これらのいずれか1種または2種以上が混合されて含まれていてもよい。

【0019】このような構成を有する非水電解液は、次のようにして電池に用いられる。ここでは、リチウム二次電池の例を挙げ、図面を参照して、以下に説明する。

【0020】図1は、本実施の形態に係る非水電解液を用いた二次電池の断面構造を表すものである。なお、図1に示したものは、いわゆるコイン型といわれるものである。この二次電池は、外装カップ11内に収容された円板状の負極12と外装缶13内に収容された円板状の正極14とが、セパレータ15を介して積層されたものである。外装カップ11および外装缶13の内部は本実施の形態に係る非水電解液16により満たされており、外装カップ11および外装缶13の周縁部は絶縁ガスケット17を介してかしめられることにより密閉されている。

【0021】負極12は、例えば、リチウムあるいはリチウムイオンまたはLi-Al合金などのリチウム合金

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を吸蔵および脱離することが可能な炭素材料を含有している。この炭素材料は、所定の温度および雰囲気にて調製されたものであり、例えば、熱分解炭素類、石油コークスもしくはピッチコークスなどのコークス類、人造黒鉛類、天然黒鉛類、アセチレンブラックなどのカーボンブラック、ガラス状炭素類、有機高分子材料焼成体あるいは炭素繊維などが用いられている。なお、有機高分子材料焼成体というのは、有機高分子材料を不活性ガス雰囲気中または真空中において500℃以上の適当な温度で焼成したものである。

【0022】正極14は、例えば、正極活性物質として、 $\text{TiS}_2$ 、 $\text{MoS}_2$ 、 $\text{NbSe}_2$ あるいはV、O、などのリチウムを含有しない金属硫化物もしくは酸化物、またはリチウムを含有するリチウム複合酸化物を含有している。特に、エネルギー密度を高くするには、Li、M、O<sub>2</sub>を主体とするリチウム複合酸化物を含んでいることが好ましい。なお、Mは1種類以上の遷移金属が好ましく、具体的には、コバルト(Co)、ニッケル(Ni)およびマンガン(Mn)のうちの少なくとも1種が好ましい。また、 $x$ は、通常、 $0.05 \leq x \leq 1.10$ の範囲内の値である。このようなリチウム複合酸化物の具体例としては、 $\text{LiCoO}_2$ 、 $\text{LiNiO}_2$ 、 $\text{Li}_x\text{Ni}_{1-x}\text{Co}_y\text{O}_2$ （但し、 $x$ および $y$ の値は電池の充放電状態によって異なり、通常、 $0 < x < 1$ 、 $0.7 < y \leq 1$ である。）あるいは $\text{LiMn}_2\text{O}_4$ などが挙げられる。

【0023】なお、このリチウム複合酸化物は、例えば、リチウムの炭酸塩、硝酸塩、酸化物あるいは水酸化物と、遷移金属の炭酸塩、硝酸塩、酸化物あるいは水酸化物とを所望の組成に応じて粉砕混合し、酸素雰囲気中において600~1000℃の範囲内の温度で焼成することにより調製される。

【0024】セパレータ15は、負極12と正極14とを隔離し、両極の接触による電流の短絡を防止しつつリチウムイオンを通過させるものであり、例えば、ポリテトラフルオロエチレン、ポリプロピレンあるいはポリエチレンなどの合成樹脂製の不織布またはセラミックフィルムまたは多孔質薄膜フィルムなどにより構成されている。

【0025】このような構成を有する二次電池は次のように作用する。

【0026】この二次電池では、充電を行うと、正極14に含まれるリチウムはイオンとなって脱離し、非水電解液16を介してセパレータ15を通過して負極12に含まれる炭素材料に吸蔵される。その後、放電を行うと、負極12に含まれる炭素材料に吸蔵されたリチウムがイオンとなって脱離し、非水電解液16を介してセパレータ15を通過して正極14に戻り吸蔵される。ここで、非水電解液16は、溶媒として化5に示したシロキサン誘導体を含んでいるので、化学的安定性が高く、難

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燃性または低蒸気圧であるために熱化学的にも優れている。よって、電流の短絡時においても気化または分解が起こりにくく、電池の破損または発火が防止され、高電圧においても優れた電池性能が示される。

【0027】このように、本実施の形態に係る非水電解液によれば、溶媒として化5に示したシロキサン誘導体を含んでいるので、化学的安定性および熱化学的安定性を高くすることができる。よって、この非水電解液を用いて電池を構成すれば、電流の短絡時に急激に大電流が流れても、非水電解液の気化または分解を抑制することができる。従って、電池の破損または発火を防止でき、安全性を向上させるとことができると共に、高電圧においても優れた電池性能を得ることができる。

【0028】また、シロキサン誘導体の温度25℃における動粘性率を5000cSt以下あるいは平均分子量を10000以下とするようにすれば、高い導電率を引\*

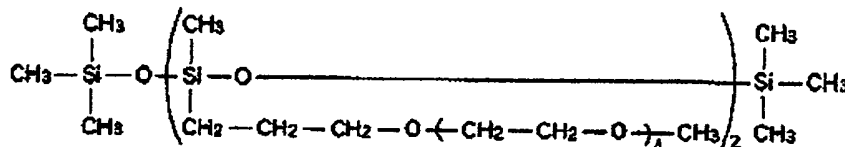
\*き出すのに充分な軽金属塩を溶解することができ、かつ軽金属イオンが移動することができる良好な非水電解液を得ることができる。

【0029】

【実施例】更に、本発明の具体的な実施例について詳細に説明する。ここでは、化6に示したシロキサン誘導体にリチウム塩として(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NLi<sub>1</sub>を添加した4種類の非水電解液を作製した。(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NLi<sub>1</sub>の添加量は表1に示したように各実施例において変化させ、シロキサン誘導体1gに対してそれぞれ実施例1では0.5mol、実施例2では1.0mol、実施例3では1.5mol、実施例4では3.0molとした。

【0030】

【化6】



【0031】

※ ※ 【表1】

	シロキサン誘導体1gに対する (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLiの添加量 (mol)	導電率 (25℃) (mS/cm)
実施例1	0.5	2.93 × 10 <sup>-1</sup>
2	1.0	4.04 × 10 <sup>-1</sup>
3	1.5	3.39 × 10 <sup>-1</sup>
4	3.0	1.03 × 10 <sup>-1</sup>

【0032】これら各実施例の非水電解液について、イオン導電度試験をそれぞれ行った。イオン導電度試験では、各非水電解液を厚さ0.145cmおよび面積0.7854cm<sup>2</sup>のステンレス板で挟んで電圧を印加し、その印加する正弦波交流電圧を記号法(複素表示)で表現したいわゆるコール・コール(Cole-Cole)プロットから導電率を求めた。得られた結果を表1に示す。なお、各実施例の非水電解液における化6に示したシロキサン誘導体の温度25℃での動粘性率は20cStであった。

【0033】これらの結果から、各実施例の非水電解液はいずれも電池に使用することができる導電性を有することが分かった。

【0034】また、更に、実施例2の非水電解液について酸化安定性試験および放電特性試験を行った。酸化安定性試験では、サイクリック・ボルタモグラムの測定して酸化安定性を調べた。測定は3電極系の電気化学セルを使用し、作用極に直径0.5mmのニッケル電極を、対極と参照極にリチウム金属をそれぞれ使用した。その際の安定な電位の範囲は、100μA/cm<sup>2</sup>の酸化電流が発生するまでとした。その結果、酸化安定電位は

4.8Vと十分に高い値が得られた。この結果から、この非水電解液によれば高電圧においても優れた電池性能を得られることが分かった。

【0035】放電特性試験では、図1に示したようなコイン型のテストセルを作製し、充放電を行った。テストセルの正極にはLiCoO<sub>2</sub>を用い、負極には炭素材料を用いた。充放電は、上限電圧を4.2V、下限電圧を3.0V、放電電流を100μAとして20サイクルまで繰り返した。その結果得られた充放電曲線を図2に示す。図2から、この非水電解液を用いた電池は十分な充放電特性を有することが分かった。よって、この非水電解液を用いれば、優れた電池性能を得られることが分かった。

【0036】すなわち、以上の結果から、各実施例の非水電解液によれば、十分な導電率が得られると共に、十分な充放電特性を得ることができ、更に、高電圧においても安定していることが分かった。よって、この非水電解液を用いれば、優れた電池性能を得ることができる。

【0037】以上、実施の形態および実施例を挙げて本発明を説明したが、本発明は上記実施の形態および各実施例に限定されるものではなく、種々変形可能である。

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例えば、上記実施の形態および各実施例においては、リチウム二次電池について説明したが、本発明は、ナトリウムあるいはアルミニウムなど他の軽金属を用いた二次電池についても同様に適用することができる。その場合、非水電解液の軽金属塩および正極の正極活性物質は、それに応じて適宜に選択される。

【0038】また、上記実施の形態においては、コイン型の二次電池について説明したが、本発明は、ボタン型、ペーパー型、角型あるいはスパイラル構造を有する筒型など他の形状のものについても同様に適用することができる。

【0039】更に、上記実施の形態においては、二次電池について説明したが、本発明は、一次電池などの他の電池にも適用することができる。

【0040】

【発明の効果】以上説明したように請求項1ないし請求項5のいずれか1に記載の非水電解液によれば、化1に示したシロキサン誘導体を含んでいるので、化学的安定性および熱化学的安定性を高くすることができる。よって、この非水電解液を用いて電池を構成すれば、電流の短絡時に急激に大電流が流れても、気化または分解を抑制することができる。従って、電池の破損または発火を防止でき、安全性を向上させることができると共に、高電圧においても優れた電池性能を得ることができるという効果を奏する。

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\*【0041】また、請求項2または請求項4に記載の非水電解液によれば、シロキサン誘導体の温度25℃における動粘性率を5000cSt以下あるいは平均分子量を10000以下とするようにしたので、高い導電率を引き出すのに十分な軽金属塩を溶解することができ、かつ軽金属イオンが移動することができる良好な非水電解液を得ることができるという効果を奏する。

【0042】また、請求項6ないし請求項10のいずれか1に記載の電池によれば、化2に示したシロキサン誘導体を含む非水電解液を備えているので、電流の短絡時に急激に大電流が流れても、非水電解液の気化または分解を抑制することができる。よって、電池の破損または発火を防止でき、安全性を向上させることができると共に、高電圧においても優れた電池性能を得ることができるという効果を奏する。

【図面の簡単な説明】

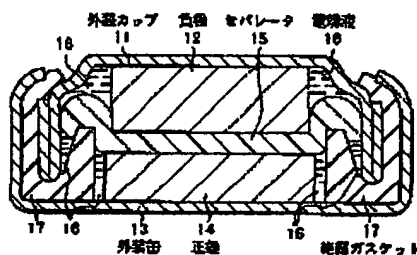
【図1】本発明の一実施の形態に係る非水電解液を用いた二次電池の構成を表す断面図である。

【図2】本発明の実施例2に係る非水電解液の放電特性試験における充放電曲線を示す特性図である。

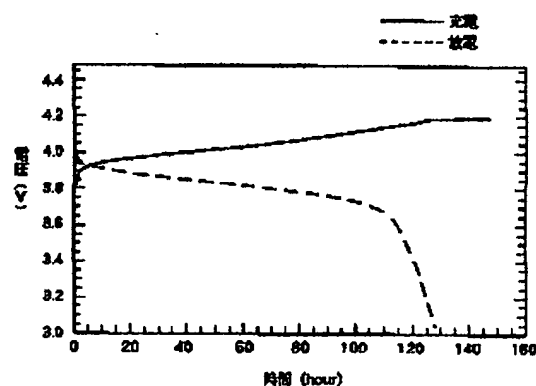
【符号の説明】

11…外装カップ、12…負極、13…外装缶、14…正極、15…セパレータ、16…電解液、17…絶縁ガasket

【図1】



【図2】



フロントページの続き

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ー株式会社内

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DH006 DK006 GQ00  
SH029 AJ07 AJ12 AK02 AK05 AL06  
AL12 AM01 AM07 AM16 EJ11  
HJ02 HJ10 HJ11 HJ20

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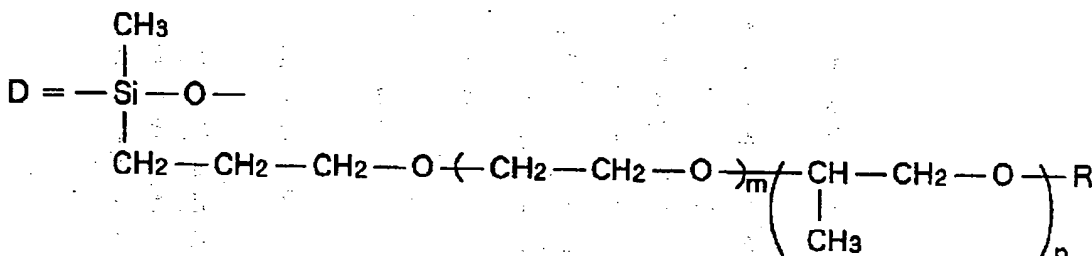
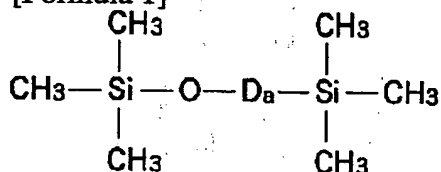
**CLAIMS**


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[Claim(s)]

[Claim 1] Nonaqueous electrolyte characterized by including the siloxane derivative shown by following \*\* 1, and at least one sort of light metal salts.

[Formula 1]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of a > 1, even if a D is the same, it may differ. Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[Claim 2] The aforementioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C being 5000 or less cSts.

[Claim 3] The aforementioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by average molecular weight being 10000 or less.

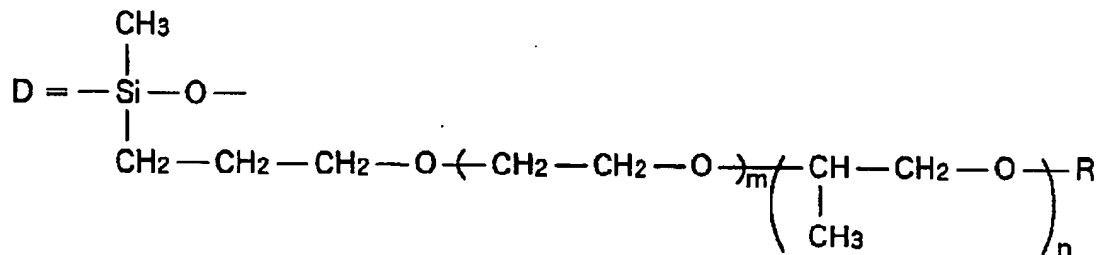
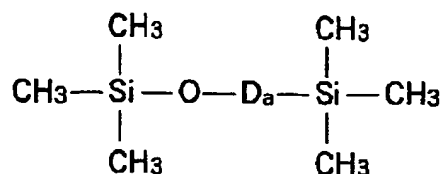
[Claim 4] The aforementioned light metal salt is nonaqueous electrolyte according to claim 1 characterized by being a lithium metal salt.

[Claim 5] Nonaqueous electrolyte according to claim 1 characterized by the conductivity in the temperature of 25 degrees C being 0.1 or more mS/cm.

[Claim 6] The cell characterized by having the separator formed between the positive electrode, the negative electrode, and the aforementioned positive electrode and the aforementioned negative electrode, and nonaqueous electrolyte containing the siloxane derivative and at least one sort of light metal salts which are shown by following \*\* 2.

[Formula 2]





(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ. Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[Claim 7] The aforementioned nonaqueous electrolyte is a cell according to claim 6 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C containing the siloxane derivative of 5000 or less cSts.

[Claim 8] The aforementioned nonaqueous electrolyte is a cell according to claim 6 characterized by average molecular weight containing 10000 or less siloxane derivative.

[Claim 9] The aforementioned nonaqueous electrolyte is a cell according to claim 6 characterized by the conductivity in the temperature of 25 degrees C being 0.1 or more mS/cm.

[Claim 10] It is the cell according to claim 6 characterized by the aforementioned negative electrode containing occlusion and the carbon material from which it can be desorbed for a lithium, a lithium alloy, or a lithium ion while the aforementioned positive electrode contains occlusion and the oxide from which it can be desorbed, or a sulfide for a lithium ion.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the cell using the nonaqueous electrolyte and it containing the light metal salt which is an electrolyte, and a solvent.

[0002]

[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, or a laptop computer, are spreading quickly. moreover, the viewpoint of an environmental problem to NO<sub>x</sub> etc. -- development of the electric vehicle which does not discharge exhaust gas in air has come to be taken up as a social technical problem The research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are actively furthered under such a situation. Since a high energy density is obtained as compared with the lead (Pb) rechargeable battery or nickel cadmium (nickel-Cd) rechargeable battery which is the conventional drainage system electrolytic-solution rechargeable battery, the rechargeable battery (lithium secondary battery) which used the lithium (Li) or the lithium ion (Li<sup>+</sup>) especially attracts great expectation.

[0003] non-aqueous solvents, such as carbonates, such as low-molecular ethylene carbonate as the electrolytic solution of this lithium secondary battery, propylene carbonate, or diethyl carbonate, -- as an electrolyte -- LiPF<sub>6</sub> etc. -- it is widely used from that [ conductivity's ] in which the lithium system electrolyte salt was dissolved being comparatively high, and being stable also in potential

[0004] However, although the lithium secondary battery using such nonaqueous electrolyte is highly efficient, since the inflammable organic solvent is used as the electrolytic solution, a problem may arise in safety. For example, the high current may have flowed and generated heat in the cell rapidly at the time of the short circuit of current, the electrolytic solution which contains an organic solvent by this may have caused evaporation or decomposition, and breakage, rupture, or ignition of a cell may have taken place for the generation of gas by this. Then, in order to prevent these conventionally, the safety practice was performed by preparing a relief valve or a current interrupting device etc. which will cleave if the pressure in a cell rises.

[0005]

[Problem(s) to be Solved by the Invention] However, since safety was secured by improving structure mechanisms, such as a relief valve, conventionally, while structure will be complicated, only the part of those structures had the problem that the size of a cell will become large. Then, to improve cell material fundamentally is desired.

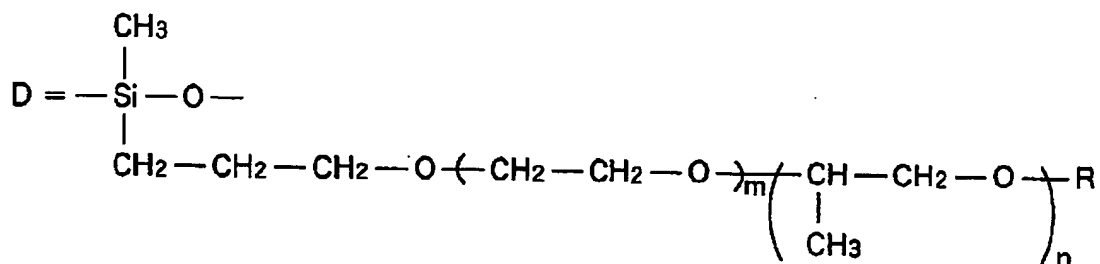
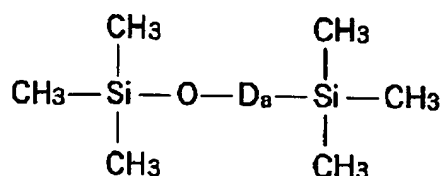
[0006] this invention was made in view of this trouble, and the 1st purpose is in offering nonaqueous electrolyte excellent in chemical stability and thermochemical stability.

[0007] Moreover, the 2nd purpose of this invention is by suppressing evaporation or decomposition of the electrolytic solution to offer the cell which prevented the breakage or ignition of a cell by generating of gas, and was excellent in the cell performance.

[0008]

[Means for Solving the Problem] The nonaqueous electrolyte by this invention contains the siloxane derivative shown by following \*\* 3, and at least one sort of light metal salts.

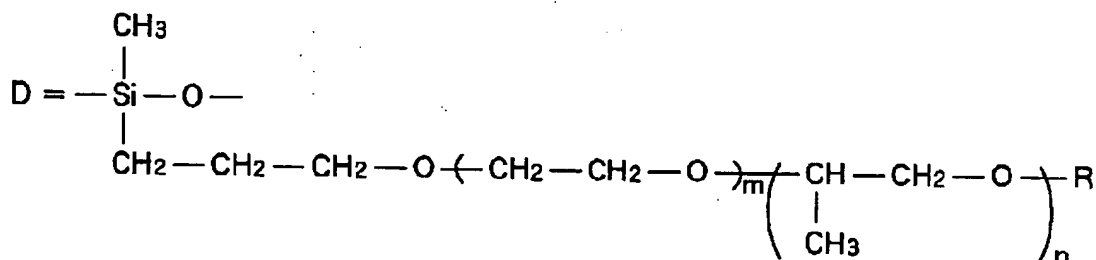
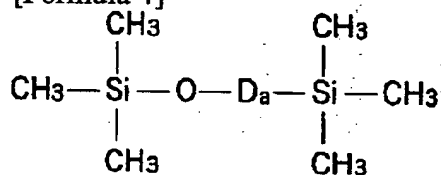
[Formula 3]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0009] The cell by this invention is equipped with the separator formed between the positive electrode, the negative electrode, and a positive electrode and a negative electrode, and the nonaqueous electrolyte containing the siloxane derivative and at least one sort of light metal salts which are shown by following \*\* 4.

[Formula 4]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0010] In the nonaqueous electrolyte by this invention, since the siloxane derivative shown in \*\* 3 is included, chemical stability is high, and since it is fire retardancy or low vapor pressure, it has the property of excelling also thermochemically. Therefore, if a cell is constituted using this nonaqueous electrolyte, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent also in the high voltage is shown.

[0011] By the cell by this invention, light metal ion moves the inside of nonaqueous electrolyte to a negative electrode from a positive electrode through separator by charge, and light metal ion moves the inside of nonaqueous electrolyte to a positive electrode from a negative electrode through separator by electric discharge. Here, since nonaqueous electrolyte contains the siloxane derivative shown in \*\* 4, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent

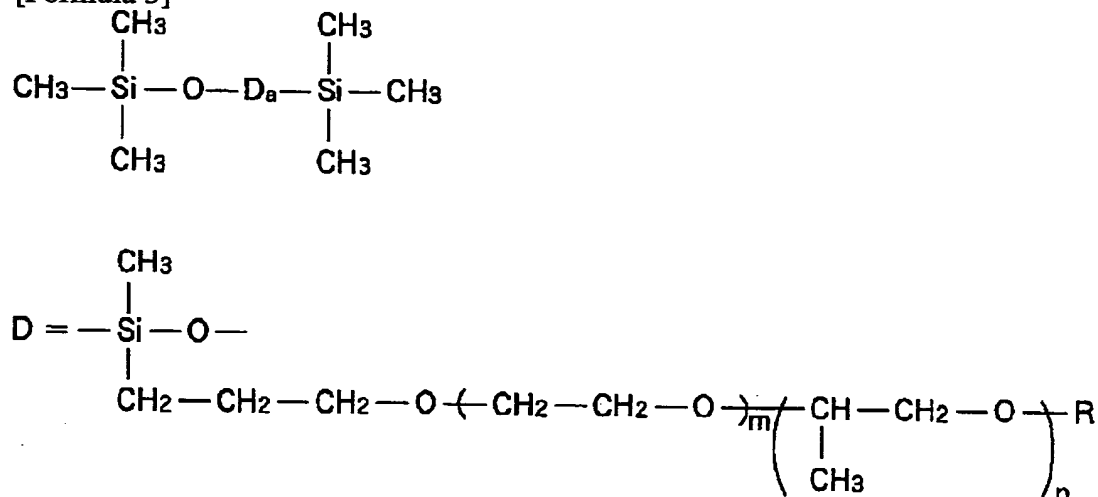
also in the high voltage is shown.

[0012]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail with reference to a drawing.

[0013] The nonaqueous electrolyte concerning the gestalt of 1 operation of this invention consists of a siloxane derivative shown in \*\* 5 which is a solvent, and at least one sort of light metal salts which are electrolytes.

[Formula 5]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0014] This siloxane derivative is a shape of chain type inorganic polymer which has the chain combination of silicon (Si) and oxygen (O) in a basic skeleton and by which the side chain which is a univalent organic machine was added to silicon. This siloxane derivative has high chemical stability, and since it is fire retardancy or low vapor pressure, it has the property of excelling also in thermochemical stability.

[0015] In addition, the coefficient of kinematic viscosity in the temperature of 25 degrees C of this siloxane derivative is 5000 or less cSts, and, as for average molecular weight, it is desirable that it is 10000 or less. It is because viscosity is comparatively low and it is required to dissolve a light metal salt, in order to use as a solvent of the electrolytic solution. These are adjusted by choosing moderately the side chain radical of D in the chemical formula shown in \*\* 5, and the number of a in a chemical formula. As for a in this chemical formula, it is desirable in that case that it is the integer of 1 to 20 within the limits.

[0016] On the other hand, there is alkali-metal salts, such as lithium salt or a sodium (Na) salt, or an aluminum (aluminum) salt as light metal salt, and it is chosen expedient according to the kind of cell which uses this nonaqueous electrolyte. In constituting a lithium cell, for example,  $\text{LiBF}_4$  and  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ , 2  $(\text{CF}_3\text{SO}_2)\text{NLi}$ ,  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$ ,  $\text{CF}_3\text{CO}_2\text{Li}$ , 2  $(\text{CF}_3\text{CO}_2)\text{NLi}$ ,  $\text{C}_6\text{F}_5\text{SO}_3\text{Li}$ ,  $\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$ , 2  $(\text{C}_2\text{F}_5\text{SO}_2)\text{NLi}$ ,  $\text{NLi}$ ,  $\text{NLi}(\text{CF}(\text{FSO}_2\text{C}_6\text{F}_4)_3\text{SO}_2)$ ,  $(\text{C}_4\text{F}_9\text{SO}_2)(\text{CF}_3\text{SO}_2)(\text{CF}_3)_2\text{NLi}$ , 3  $(\text{CF}_3\text{SO}_2)\text{CLi}$ , 4  $(3\text{C}_6\text{F}_3_2(\text{CF}_3)-5)\text{BLi}$  or  $\text{LiCF}_3$ , and  $\text{LiAlCl}_4$  (2  $\text{CHOSO}_2$ )<sub>4</sub> etc. -- lithium salt is used

[0017] In addition, as for the conductivity in the temperature of 25 degrees C of this nonaqueous electrolyte, it is desirable that they are 0.1 or more mS/cm, and it is adjusted by the kind of light metal salt, or its concentration.

[0018] Moreover, in addition to the siloxane derivative, this nonaqueous electrolyte may contain other solvents. As other solvents, there is propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, a propionitrile, an anisole, acetic ester, or propionic-acid ester, and any these one sort or

two sorts or more may be mixed and contained, for example.

[0019] The nonaqueous electrolyte which has such composition is used for a cell as follows. Here, the example of a lithium secondary battery is given and it explains below with reference to a drawing.

[0020] Drawing 1 expresses the cross-section structure of the rechargeable battery using the nonaqueous electrolyte concerning the gestalt of this operation. In addition, what was shown in drawing 1 is called so-called coin type. The laminating of the disc-like negative electrode 12 by which this rechargeable battery was held in the sheathing cup 11, and the disc-like positive electrode 14 held in the sheathing can 13 is carried out through separator 15. the interior of the sheathing cup 11 and the sheathing can 13 is filled by the nonaqueous electrolyte 16 concerning the gestalt of this operation -- having -- \*\*\*\* -- the periphery section of the sheathing cup 11 and the sheathing can 13 -- an insulating gasket 17 -- minding -- it is sealed by being closed

[0021] The negative electrode 12 contains occlusion and the carbon material which can be \*\*\*\*ed for lithium alloys, such as a lithium, a lithium ion, or an Li-aluminum alloy. This carbon material is prepared in predetermined temperature and predetermined atmosphere, for example, carbon black, such as corks, such as pyrolytic carbons, petroleum coke, or pitch coke, artificial graphites, natural graphites, and acetylene black, glassy carbons, the organic polymeric-materials baking object, or the carbon fiber is used. In addition, an organic polymeric-materials baking object calcinates organic polymeric materials at the suitable temperature of 500 degrees C or more in inert gas atmosphere or a vacuum.

[0022] a positive electrode 14 -- as a positive active material --  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{NbSe}_2$  Or  $\text{V}_2\text{O}_5$  etc. -- the metallic sulfide which does not contain a lithium, the oxide, or the lithium multiple oxide containing a lithium is contained In order to make an energy density high especially, it is  $\text{Li}_x\text{MO}_2$ . It is desirable that the lithium multiple oxide made into a subject is included. In addition, one or more kinds of transition metals of M are desirable, and, specifically, its at least one sort in cobalt (Co), nickel (nickel), and manganese (Mn) is desirable. Moreover, x is usually the value of  $0.05 \leq x \leq 1.10$  within the limits. as the example of such a lithium multiple oxide --  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ , or (however, the value of x and y changes with charge-and-discharge states of a cell, and are usually  $0 < x < 1$  and  $0.7 < y \leq 1$ .)  $\text{LiMn}_2\text{O}_4$  etc. -- it is mentioned

[0023] In addition, this lithium multiple oxide carries out trituration mixture according to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and the carbonate of transition metals, a nitrate, an oxide or a hydroxide, and is prepared by calcinating in oxygen atmosphere at the temperature within the limits of 600-1000 degrees C.

[0024] Separator 15 isolates a negative electrode 12 and a positive electrode 14, it passes a lithium ion, preventing the short circuit of the current by contact of two poles, and is constituted by a nonwoven fabric, a ceramic film, or porosity thin film films made of synthetic resin, such as a polytetrafluoroethylene, polypropylene, or polyethylene, etc.

[0025] The rechargeable battery which has such composition acts as follows.

[0026] In this rechargeable battery, if it charges, it will become ion, and will \*\*\*\* and occlusion of the lithium contained in a positive electrode 14 will be carried out to the carbon material which passes separator 15 through nonaqueous electrolyte 16, and is contained in a negative electrode 12. Then, if it discharges, it will become ion and will \*\*\*\*, and separator 15 is passed through nonaqueous electrolyte 16, the lithium by which occlusion was carried out to the carbon material contained in a negative electrode 12 will return to a positive electrode 14, and occlusion will be carried out. Here, since the siloxane derivative shown in \*\* 5 as a solvent is included, nonaqueous electrolyte 16 has high chemical stability, and since it is fire retardancy or low vapor pressure, it is thermochemically excellent [ nonaqueous electrolyte ]. Therefore, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent also in the high voltage is shown.

[0027] Thus, since the siloxane derivative shown in \*\* 5 as a solvent is included according to the nonaqueous electrolyte concerning the gestalt of this operation, chemical stability and thermochemical stability can be made high. Therefore, if a cell is constituted using this nonaqueous electrolyte, even if a high current flows rapidly at the time of the short circuit of current, evaporation

or decomposition of nonaqueous electrolyte can be suppressed. Therefore, breakage or ignition of a cell can be prevented, and while being able to \*\* as if safety is raised, the cell performance which was excellent also in the high voltage can be obtained.

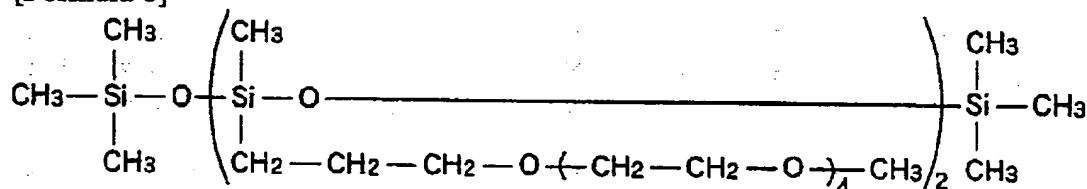
[0028] Moreover, if it is made to make 5000 or less cSts or average molecular weight for the coefficient of kinematic viscosity in the temperature of 25 degrees C of a siloxane derivative or less into 10000, the good nonaqueous electrolyte which can dissolve enough light metal salts to pull out high conductivity, and light metal ion can move can be obtained.

[0029]

[Example] Furthermore, the concrete example of this invention is explained in detail. Here, four kinds of nonaqueous electrolyte which added 2 NLi as lithium salt (CF<sub>3</sub>SO<sub>2</sub>) to the siloxane derivative shown in \*\* 6 was produced. (CF<sub>3</sub>SO<sub>2</sub>) It was made to change in each example, as the addition of 2 NLi was shown in Table 1, and to 1g of siloxane derivatives, in the example 1, it could be as 1.5 mols in 1.0 mols and the example 3, and could be [ the example 3 ] 3.0 mols by 0.5 mols and the example 2, respectively.

[0030]

[Formula 6]



[0031]

[Table 1]

	シロキサン誘導体 1g に対する (CF <sub>3</sub> SO <sub>2</sub> ) 2NLi の添加量 (mol)	導電率 (25℃) (mS/cm)
実施例 1	0.5	$2.93 \times 10^{-1}$
2	1.0	$4.04 \times 10^{-1}$
3	1.5	$3.39 \times 10^{-1}$
4	3.0	$1.03 \times 10^{-1}$

[0032] About the nonaqueous electrolyte of each [ these ] example, the ion conductivity examination was performed, respectively. By ion conductivity examination, it is each nonaqueous electrolyte the thickness of 0.145cm, and an area of 0.7854cm<sup>2</sup> It inserted with the stainless steel board, voltage was impressed, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). The obtained result is shown in Table 1. In addition, coefficients of kinematic viscosity with a temperature [ of the siloxane derivative shown in \*\* 6 in the nonaqueous electrolyte of each example ] of 25 degrees C were 20cSt(s).

[0033] These results showed that each nonaqueous electrolyte of each example had the conductivity which can be used for a cell.

[0034] Furthermore, the oxidation stability examination and the electric discharge characteristic test were performed about the nonaqueous electrolyte of an example 2. In the oxidation stability examination, the cyclic voltamogram was measured and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, the nickel electrode with a diameter of 0.5mm was used for the operation pole, and the lithium metal was used for the counter electrode and the reference pole, respectively. The range of the stable potential in that case is 100microA/cm<sup>2</sup>. It carried out until an oxidation current occurred. Consequently, the value with oxidization stable potential as high enough as 4.8V was acquired. This result showed that the cell performance which was excellent also in the high voltage according to this nonaqueous electrolyte could be obtained.

[0035] In the electric discharge characteristic test, the coin type test cell as shown in drawing 1 was produced, and charge and discharge were performed. In the positive electrode of a test cell, it is

LiCoO<sub>2</sub>. It used and the carbon material was used for the negative electrode. Charge and discharge set 4.2V and minimum voltage to 3.0V, set the discharge current to 100microA, and upper limit voltage was repeated up to 20 cycles. The charge-and-discharge curve obtained as a result is shown in drawing 2. Drawing 2 showed that the cell using this nonaqueous electrolyte had sufficient charge-and-discharge property. Therefore, when using this nonaqueous electrolyte, it turns out that the outstanding cell performance can be obtained.

[0036] That is, the above result showed that could acquire sufficient charge-and-discharge property and it was stable also in the high voltage further while sufficient conductivity is obtained according to the nonaqueous electrolyte of each example. Therefore, if this nonaqueous electrolyte is used, the outstanding cell performance can be obtained.

[0037] As mentioned above, although the gestalt and example of operation were given and this invention was explained, this invention is not limited to the gestalt and each example of the above-mentioned implementation, and can deform variously. For example, in the gestalt and each example of the above-mentioned implementation, although the lithium secondary battery was explained, this invention is applicable about the rechargeable battery which used other light metals, such as sodium or aluminum, similarly. In this case, the light metal salt of nonaqueous electrolyte and the positive active material of a positive electrode are suitably chosen according to it.

[0038] Moreover, in the gestalt of the above-mentioned implementation, although the coin type rechargeable battery was explained, this invention is applicable about the thing of other configurations, such as telescopic [ which has a button type, a paper type, a square shape, or spiral structure ], similarly.

[0039] Furthermore, in the gestalt of the above-mentioned implementation, although the rechargeable battery was explained, this invention is applicable to other cells, such as a primary cell.

[0040]

[Effect of the Invention] Since the siloxane derivative shown in \*\* 1 is included according to nonaqueous electrolyte given in any 1 of a claim 1 or the claims 5 as explained above, chemical stability and thermochemical stability can be made high. Therefore, if a cell is constituted using this nonaqueous electrolyte, even if a high current flows rapidly at the time of the short circuit of current, evaporation or decomposition can be suppressed. Therefore, breakage or ignition of a cell can be prevented, and while being able to \*\* as if safety is raised, the effect that the cell performance which was excellent also in the high voltage can be obtained is done so.

[0041] Moreover, according to nonaqueous electrolyte according to claim 2 or 4, since it was made to make 5000 or less cSts or average molecular weight for the coefficient of kinematic viscosity in the temperature of 25 degrees C of a siloxane derivative or less into 10000, the effect that the good nonaqueous electrolyte which can dissolve enough light metal salts to pull out high conductivity, and light metal ion can move can be obtained is done so.

[0042] Moreover, since it has nonaqueous electrolyte containing the siloxane derivative shown in \*\* 2 according to the cell given in any 1 of a claim 6 or the claims 10, even if a high current flows rapidly at the time of the short circuit of current, evaporation or decomposition of nonaqueous electrolyte can be suppressed. Therefore, while being able to prevent breakage or ignition of a cell and being able to raise safety, the effect that the cell performance which was excellent also in the high voltage can be obtained is done so.

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TECHNICAL FIELD

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[The technical field to which invention belongs] this invention relates to the cell using the nonaqueous electrolyte and it containing the light metal salt which is an electrolyte, and a solvent.

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[Translation done.]

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**PRIOR ART**

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[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, or a laptop computer, are spreading quickly. moreover, the viewpoint of an environmental problem to NO<sub>x</sub> etc. -- development of the electric vehicle which does not discharge exhaust gas in air has come to be taken up as a social technical problem The research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are actively furthered under such a situation. Since a high energy density is obtained as compared with the lead (Pb) rechargeable battery or nickel cadmium (nickel-Cd) rechargeable battery which is the conventional drainage system electrolytic-solution rechargeable battery, the rechargeable battery (lithium secondary battery) which used the lithium (Li) or the lithium ion (Li<sup>+</sup>) especially attracts great expectation.

[0003] non-aqueous solvents, such as carbonates, such as low-molecular ethylene carbonate as the electrolytic solution of this lithium secondary battery, propylene carbonate, or diethyl carbonate, -- as an electrolyte -- LiPF<sub>6</sub> etc. -- it is widely used from that [ conductivity's ] in which the lithium system electrolyte salt was dissolved being comparatively high, and being stable also in potential

[0004] However, although the lithium secondary battery using such nonaqueous electrolyte is highly efficient, since the inflammable organic solvent is used as the electrolytic solution, a problem may arise in safety. For example, the high current may have flowed and generated heat in the cell rapidly at the time of the short circuit of current, the electrolytic solution which contains an organic solvent by this may have caused evaporation or decomposition, and breakage, a burst, or ignition of a cell may have taken place for the generation of gas by this. Then, in order to prevent these conventionally, the safety practice was performed by preparing a relief valve or a current interrupting device etc. which will cleave if the pressure in a cell rises.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] Since the siloxane derivative shown in \*\* 1 is included according to nonaqueous electrolyte given in any 1 of a claim 1 or the claims 5 as explained above, chemical stability and thermochemical stability can be made high. Therefore, if a cell is constituted using this nonaqueous electrolyte, even if a high current flows rapidly at the time of the short circuit of current, evaporation or decomposition can be suppressed. Therefore, breakage or ignition of a cell can be prevented, and while being able to \*\* as if safety is raised, the effect that the cell performance which was excellent also in the high voltage can be obtained is done so.

[0041] Moreover, according to nonaqueous electrolyte according to claim 2 or 4, since it was made to make 5000 or less cSts or average molecular weight for the coefficient of kinematic viscosity in the temperature of 25 degrees C of a siloxane derivative or less into 1'0000, the effect that the good nonaqueous electrolyte which can dissolve enough light metal salts to pull out high conductivity, and light metal ion can move can be obtained is done so.

[0042] Moreover, since it has nonaqueous electrolyte containing the siloxane derivative shown in \*\* 2 according to the cell given in any 1 of a claim 6 or the claims 10, even if a high current flows rapidly at the time of the short circuit of current, evaporation or decomposition of nonaqueous electrolyte can be suppressed. Therefore, while being able to prevent breakage or ignition of a cell and being able to raise safety, the effect that the cell performance which was excellent also in the high voltage can be obtained is done so.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] However, since safety was secured by improving structure mechanisms, such as a relief valve, conventionally, while structure will be complicated, only the part of those structures had the problem that the size of a cell will become large. Then, to improve cell material fundamentally is desired.

[0006] this invention was made in view of this trouble, and the 1st purpose is in offering nonaqueous electrolyte excellent in chemical stability and thermochemical stability.

[0007] Moreover, the 2nd purpose of this invention is by suppressing evaporation or decomposition of the electrolytic solution to offer the cell which prevented the breakage or ignition of a cell by generating of gas, and was excellent in the cell performance.

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[Translation done.]

## \* NOTICES \*

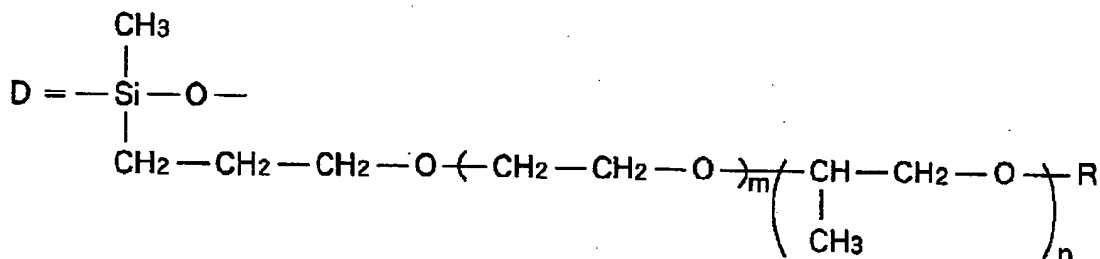
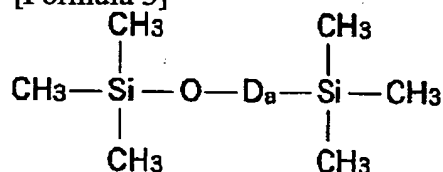
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## MEANS

[Means for Solving the Problem] The nonaqueous electrolyte by this invention contains the siloxane derivative shown by following \*\* 3, and at least one sort of light metal salts.

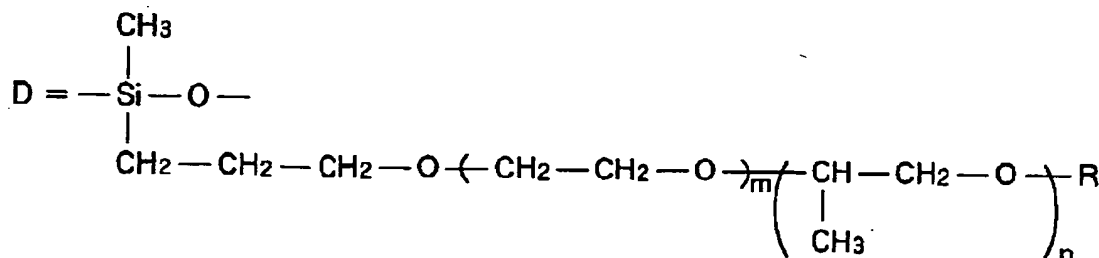
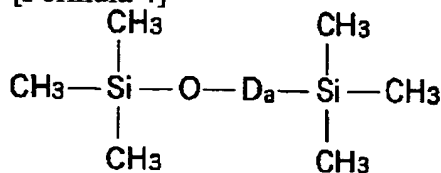
[Formula 3]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of a > 1, even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0009] The cell by this invention is equipped with the separator formed between the positive electrode, the negative electrode, and a positive electrode and a negative electrode, and the nonaqueous electrolyte containing the siloxane derivative and at least one sort of light metal salts which are shown by following \*\* 4.

[Formula 4]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses

the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0010] In the nonaqueous electrolyte by this invention, since the siloxane derivative shown in \*\* 3 is included, chemical stability is high, and since it is fire retardancy or low vapor pressure, it has the property of excelling also thermochemically. Therefore, if a cell is constituted using this nonaqueous electrolyte, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent also in the high voltage is shown.

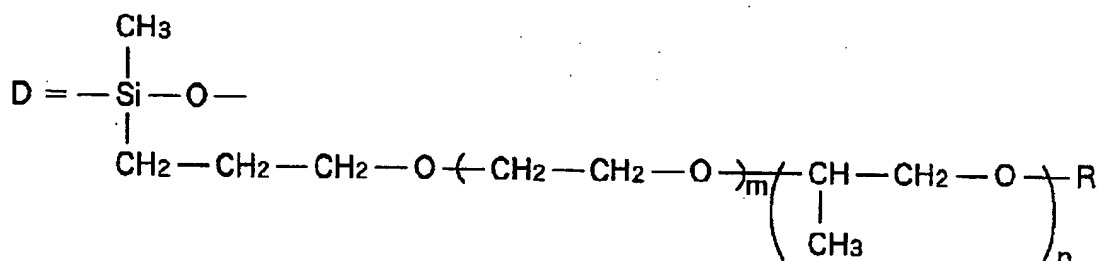
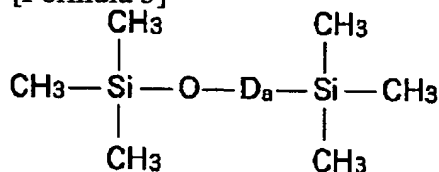
[0011] By the cell by this invention, light metal ion moves the inside of nonaqueous electrolyte to a negative electrode from a positive electrode through separator by charge, and light metal ion moves the inside of nonaqueous electrolyte to a positive electrode from a negative electrode through separator by electric discharge. Here, since nonaqueous electrolyte contains the siloxane derivative shown in \*\* 4, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent also in the high voltage is shown.

[0012]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail with reference to a drawing.

[0013] The nonaqueous electrolyte concerning the gestalt of 1 operation of this invention consists of a siloxane derivative shown in \*\* 5 which is a solvent, and at least one sort of light metal salts which are electrolytes.

[Formula 5]



(a expresses the integer of 1 to 50 among a formula, m expresses the integer of 0 to 40, n expresses the integer of 0 to 40, and R expresses a hydrogen atom or an alkyl group.) in addition, at the time of  $a > 1$ , even if a D is the same, it may differ Moreover, the hydrogen atom contained in D and R may be replaced by the halogen atom.

[0014] This siloxane derivative is a shape of chain type inorganic polymer which has the chain combination of silicon (Si) and oxygen (O) in a basic skeleton and by which the side chain which is a univalent organic machine was added to silicon. This siloxane derivative has high chemical stability, and since it is fire retardancy or low vapor pressure, it has the property of excelling also in thermochemical stability.

[0015] In addition, the coefficient of kinematic viscosity in the temperature of 25 degrees C of this siloxane derivative is 5000 or less cSts, and, as for average molecular weight, it is desirable that it is 10000 or less. It is because viscosity is comparatively low and it is required to dissolve a light metal salt, in order to use as a solvent of the electrolytic solution. These are adjusted by choosing moderately the side chain radical of D in the chemical formula shown in \*\* 5, and the number of a in a chemical formula. As for a in this chemical formula, it is desirable in that case that it is the integer of 1 to 20 within the limits.

[0016] On the other hand, there is alkali-metal salts, such as lithium salt or a sodium (Na) salt, or an aluminum (aluminum) salt as light metal salt, and it is chosen expedient according to the kind of cell which uses this nonaqueous electrolyte. In constituting a lithium cell, for example,  $\text{LiBF}_4$  and  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ , 2  $(\text{CF}_3\text{SO}_2)\text{NLi}$ ,  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$ ,  $\text{CF}_3\text{CO}_2\text{Li}$ , 2  $(\text{CF}_3\text{CO}_2)\text{NLi}$ ,  $\text{C}_6\text{F}_5\text{SO}_3\text{Li}$ ,  $\text{C}_8\text{F}_{17}\text{SO}_3\text{Li}$ , 2  $(\text{C}_2\text{F}_5\text{SO}_2)\text{NLi}$ ,  $\text{NLi}$ ,  $\text{NLi}(\text{CF}(\text{FSO}_2\text{C}_6\text{F}_4)_3\text{SO}_2)$ ,  $(\text{C}_4\text{F}_9\text{SO}_2)(\text{CF}_3\text{SO}_2)(\text{CF}_3)_2\text{NLi}$ , 3  $(\text{CF}_3\text{SO}_2)\text{CLi}$ , 4  $(3\text{C}_6\text{F}_3)_2(\text{CF}_3)_5\text{BLi}$  or  $\text{LiCF}_3$ , and  $\text{LiAlCl}_2(\text{CH}_3\text{SO}_2)_4$  etc. -- lithium salt is used

[0017] In addition, as for the conductivity in the temperature of 25 degrees C of this nonaqueous electrolyte, it is desirable that they are 0.1 or more mS/cm, and it is adjusted by the kind of light metal salt, or its concentration.

[0018] Moreover, in addition to the siloxane derivative, this nonaqueous electrolyte may contain other solvents. As other solvents, there is propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, a propionitrile, an anisole, acetic ester, or propionic-acid ester, and any these one sort or two sorts or more may be mixed and contained, for example.

[0019] The nonaqueous electrolyte which has such composition is used for a cell as follows. Here, the example of a lithium secondary battery is given and it explains below with reference to a drawing.

[0020] Drawing 1 expresses the cross-section structure of the rechargeable battery using the nonaqueous electrolyte concerning the gestalt of this operation. In addition, what was shown in drawing 1 is called so-called coin type. The laminating of the disc-like negative electrode 12 by which this rechargeable battery was held in the sheathing cup 11, and the disc-like positive electrode 14 held in the sheathing can 13 is carried out through separator 15. the interior of the sheathing cup 11 and the sheathing can 13 is filled by the nonaqueous electrolyte 16 concerning the gestalt of this operation -- having -- \*\*\*\* -- the periphery section of the sheathing cup 11 and the sheathing can 13 -- an insulating gasket 17 -- minding -- it is sealed by being closed

[0021] The negative electrode 12 contains occlusion and the carbon material which can be \*\*\*\*ed for lithium alloys, such as a lithium, a lithium ion, or an Li-aluminum alloy. This carbon material is prepared in predetermined temperature and predetermined atmosphere, for example, carbon black, such as corks, such as pyrolytic carbons, petroleum coke, or pitch coke, artificial graphites, natural graphites, and acetylene black, glassy carbons, the organic polymeric-materials baking object, or the carbon fiber is used. In addition, an organic polymeric-materials baking object calcinates organic polymeric materials at the suitable temperature of 500 degrees C or more in inert gas atmosphere or a vacuum.

[0022] a positive electrode 14 -- as a positive active material --  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{NbSe}_2$  Or  $\text{V}_2\text{O}_5$  etc. -- the metallic sulfide which does not contain a lithium, the oxide, or the lithium multiple oxide containing a lithium is contained In order to make an energy density high especially, it is  $\text{Li}_x\text{MO}_2$ . It is desirable that the lithium multiple oxide made into a subject is included. In addition, one or more kinds of transition metals of M are desirable, and, specifically, its at least one sort in cobalt (Co), nickel (nickel), and manganese (Mn) is desirable. Moreover, x is usually the value of  $0.05 \leq x \leq 1.10$  within the limits. as the example of such a lithium multiple oxide --  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ , or (however, the value of x and y changes with charge-and-discharge states of a cell, and are usually  $0 < x < 1$  and  $0.7 < y \leq 1$ .)  $\text{LiMn}_2\text{O}_4$  etc. -- it is mentioned

[0023] In addition, this lithium multiple oxide carries out trituration mixture according to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and the carbonate of transition metals, a nitrate, an oxide or a hydroxide, and is prepared by calcinating in oxygen atmosphere at the temperature within the limits of 600-1000 degrees C.

[0024] Separator 15 isolates a negative electrode 12 and a positive electrode 14, it passes a lithium ion, preventing the short circuit of the current by contact of two poles, and is constituted by a nonwoven fabric, a ceramic film, or porosity thin film films made of synthetic resin, such as a polytetrafluoroethylene, polypropylene, or polyethylene, etc.

[0025] The rechargeable battery which has such composition acts as follows.

[0026] In this rechargeable battery, if it charges, it will become ion, and will \*\*\*\* and occlusion of the lithium contained in a positive electrode 14 will be carried out to the carbon material which passes separator 15 through nonaqueous electrolyte 16, and is contained in a negative electrode 12. Then, if it discharges, it will become ion and will \*\*\*\*, and separator 15 is passed through nonaqueous electrolyte 16, the lithium by which occlusion was carried out to the carbon material contained in a negative electrode 12 will return to a positive electrode 14, and occlusion will be carried out. Here, since the siloxane derivative shown in \*\* 5 as a solvent is included, nonaqueous electrolyte 16 has high chemical stability, and since it is fire retardancy or low vapor pressure, it is thermochemically excellent [ nonaqueous electrolyte ]. Therefore, evaporation or decomposition cannot take place easily at the time of the short circuit of current, breakage or ignition of a cell is prevented, and the cell performance which was excellent also in the high voltage is shown.

[0027] Thus, since the siloxane derivative shown in \*\* 5 as a solvent is included according to the nonaqueous electrolyte concerning the gestalt of this operation, chemical stability and thermochemical stability can be made high. Therefore, if a cell is constituted using this nonaqueous electrolyte, even if a high current flows rapidly at the time of the short circuit of current, evaporation or decomposition of nonaqueous electrolyte can be suppressed. Therefore, breakage or ignition of a cell can be prevented, and while being able to \*\* as if safety is raised, the cell performance which was excellent also in the high voltage can be obtained.

[0028] Moreover, if it is made to make 5000 or less cSts or average molecular weight for the coefficient of kinematic viscosity in the temperature of 25 degrees C of a siloxane derivative or less into 10000, the good nonaqueous electrolyte which can dissolve enough light metal salts to pull out high conductivity, and light metal ion can move can be obtained.

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[Translation done.]

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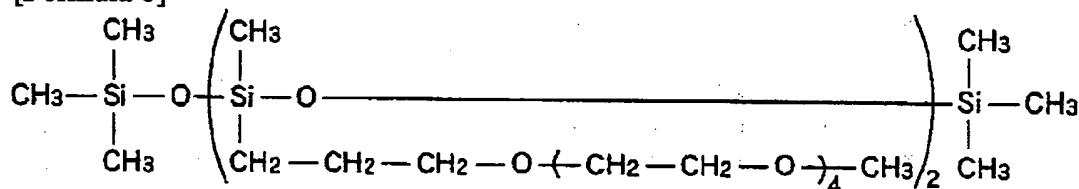
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## EXAMPLE

[Example] Furthermore, the concrete example of this invention is explained in detail. Here, four kinds of nonaqueous electrolyte which added 2 NLi as lithium salt ( $\text{CF}_3\text{SO}_2$ ) to the siloxane derivative shown in \*\* 6 was produced. ( $\text{CF}_3\text{SO}_2$ ) It was made to change in each example, as the addition of 2 NLi was shown in Table 1, and to 1g of siloxane derivatives, in the example 1, it could be as 1.5 mols in 1.0 mols and the example 3, and could be [ the example 3 ] 3.0 mols by 0.5 mols and the example 2, respectively.

[0030]

[Formula 6]



[0031]

[Table 1]

	シロキサン誘導体 1g に対する ( $\text{CF}_3\text{SO}_2$ ) 2NLi の添加量 (mol)	導電率 (25℃) (mS/cm)
実施例 1	0.5	$2.93 \times 10^{-1}$
2	1.0	$4.04 \times 10^{-1}$
3	1.5	$3.39 \times 10^{-1}$
4	3.0	$1.03 \times 10^{-1}$

[0032] About the nonaqueous electrolyte of each [ these ] example, the ion conductivity examination was performed, respectively. By ion conductivity examination, it is each nonaqueous electrolyte the thickness of 0.145cm, and an area of 0.7854cm<sup>2</sup> It inserted with the stainless steel board, voltage was impressed, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). The obtained result is shown in Table 1. In addition, coefficients of kinematic viscosity with a temperature [ of the siloxane derivative shown in \*\* 6 in the nonaqueous electrolyte of each example ] of 25 degrees C were 20cSt(s).

[0033] These results showed that each nonaqueous electrolyte of each example had the conductivity which can be used for a cell.

[0034] Furthermore, the oxidation stability examination and the electric discharge characteristic test were performed about the nonaqueous electrolyte of an example 2. In the oxidation stability examination, the cyclic voltamogram was measured and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, the nickel electrode with a diameter of 0.5mm was used for the operation pole, and the lithium metal was used for the counter electrode and the reference pole, respectively. The range of the stable potential in that case is 100microA/cm<sup>2</sup>. It carried out until an oxidation current occurred. Consequently, the value with oxidization stable potential as high enough as 4.8V was acquired. This result showed that the cell



performance which was excellent also in the high voltage according to this nonaqueous electrolyte could be obtained.

[0035] In the electric discharge characteristic test, the coin type test cell as shown in drawing 1 was produced, and charge and discharge were performed. In the positive electrode of a test cell, it is  $\text{LiCoO}_2$ . It used and the carbon material was used for the negative electrode. Charge and discharge set 4.2V and minimum voltage to 3.0V, set the discharge current to 100microA, and upper limit voltage was repeated up to 20 cycles. The charge-and-discharge curve obtained as a result is shown in drawing 2. Drawing 2 showed that the cell using this nonaqueous electrolyte had sufficient charge-and-discharge property. Therefore, when using this nonaqueous electrolyte, it turns out that the outstanding cell performance can be obtained.

[0036] That is, the above result showed that could acquire sufficient charge-and-discharge property and it was stable also in the high voltage further while sufficient conductivity is obtained according to the nonaqueous electrolyte of each example. Therefore, if this nonaqueous electrolyte is used, the outstanding cell performance can be obtained.

[0037] As mentioned above, although the gestalt and example of operation were given and this invention was explained, this invention is not limited to the gestalt and each example of the above-mentioned implementation, and can deform variously. For example, in the gestalt and each example of the above-mentioned implementation, although the lithium secondary battery was explained, this invention is applicable about the rechargeable battery which used other light metals, such as sodium or aluminum, similarly. In this case, the light metal salt of nonaqueous electrolyte and the positive active material of a positive electrode are suitably chosen according to it.

[0038] Moreover, in the gestalt of the above-mentioned implementation, although the coin type rechargeable battery was explained, this invention is applicable about the thing of other configurations, such as telescopic [ which has a button type, a paper type, a square shape, or spiral structure ], similarly.

[0039] Furthermore, in the gestalt of the above-mentioned implementation, although the rechargeable battery was explained, this invention is applicable to other cells, such as a primary cell.

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** It is a cross section showing the composition of the rechargeable battery using the nonaqueous electrolyte concerning the gestalt of 1 operation of this invention.

**[Drawing 2]** It is the property view showing the charge-and-discharge curve in the electric discharge characteristic test of the nonaqueous electrolyte concerning the example 2 of this invention.

**[Description of Notations]**

11 [ -- A sheathing can, 14 / -- A positive electrode, 15 / -- Separator, 16 / -- The electrolytic solution, 17 / -- Insulating gasket ] -- A sheathing cup, 12 -- A negative electrode, 13

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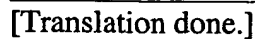
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[Drawing 1]



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